ANALYTICAL METHOD

TITLE: Ion Chromatography

DEPARTMENT: Inorganic – Wet Chemistry

APPLICATION: Anions in drinking and surface waters, and groundwater.

REFERENCES: EPA Method 300.0, Determination of Inorganic Anions by Ion Chromatography, Revision 2.1, August 1993.

Test Methods for Evaluating Solid Wastes
SW-846 Method 9056 (3rd Ed., Revision 0, September 1994)

PROCEDURE SUMMARY:

Method is used to determine Bromide, Fluoride, Chloride, Nitrite, Nitrate, and Sulfate in groundwater and surface water by use of an Ion Chromatograph.

APPROVED BY:

Michael J. Helmann
Wet Chemistry Supervisor — Date: 12/27/01

Julie A. Trivedi
Quality Assurance Officer — Date: 12/27/01

Glen A. Coder
Laboratory Manager — Date: 12/31/01

Annual Review

Date:					
Initials:					

SAMPLE HANDLING AND PRESERVATION:

Sample can be collected in glass or plastic. Samples need to be unpreserved. Sample holding times: NO_2, NO_3: 48 hours; Br, F, Cl, SO_4: 28 days.

INTERFERENCES:

Samples that contain particles larger than 0.45 microns and reagents solutions that contain particles larger than 0.20 microns require filtration to prevent damage to the instrument column or flow system.

APPARATUS AND MATERIALS:

DX – 120 Ion Chromatograph
5.0 mL sample vials and filter caps
Volumetric flasks: 100 mL, 1000 mL
Pipettors: adjustable and fixed volume (3.0, 1.5, 1.0, 0.10, 0.050, 0.010 mL)

REAGENTS AND STANDARDS:

NOTE: All solutions must be made with Milli-Q® water.

Prepare Eluent:

Dilute 10 mL of concentrated eluent to 1 L with Milli-Q® water.

Prepare Anion Calibration Standards:

Dilute 3.0, 2.5, 1.5, 1.0, 0.10, and 0.020 mL of 1000 ppm APG Standard of each of the following anions (Br, F, Cl, NO_2, NO_3, SO_4) in 100 mL volumetric with Milli-Q® water to make 30, 25, 15, 10, 1.0, 0.20 ppm standard solutions. Prepare standards weekly, except for NO_2 and those < 1 ppm which are prepared fresh daily.

Prepare Anion Check Standard:

Dilute 1.5 mL of 1000 ppm APG Standard of each of the following anions (Br, F, Cl, NO_2, NO_3, SO_4) in 100 mL volumetric with Milli-Q® water to make a 15 ppm standard. Source of standard should be of a different lot than that of calibration standards. Prepare weekly, except for NO_2, which is prepared fresh daily.

PROCEDURE:

1. Execute PeakNet.
2. Click on "Run Method".
3. Open method file: "Startup".
4. Run manual baseline until stable, usually 10 minutes.

5. Open "Schedule" from PeakNet main menu.

6. Type in analytical run you wish to perform:

    a. For calibration standards, be sure to include "sample type" as calibration std and "level" as: Cal30.0= level 1, Cal25.0 = level 2, Cal15.0 = level 3, Cal10.0 = level 4, Cal1.0 = level 5, Cal0.2 = level 6 and Cal0.0 = level 7.

    b. ICV, ICB, CCV, CCB: Sample type is "check std". CCV, ICV = level 1 and CCB, ICB = level 2.

    c. All others need sample type "sample".

    d. Enter Method: En Chem Anions.met (Br, CL, F, NO_2, NO_3, SO_4) for IC "A", or EnChem Anions B for IC "B".

    e. Enter data file: yymmdd A or B.

    f. Save schedule: yymmdd A or B.

    g. After last CCB enter sample "shutdown" with Method: shutdown.met.

7. From run window: Load schedule:

    a. Click on mode tab.

    b. Click on "run via external signal".

8. Load autosampler.

    a. Pour 5 mL of sample into each vial.

    b. Seat filter cap so top of cap is even with top of vial.

9. Press run/hold button of autosampler.

10. Once analytical run has completed, go to PeakNet main menu and open "Optimize".

11. Each sample produces it's own .dat file and chromatograph. Open each file in the optimize window, check and correct peak naming and void volumes. Excess peaks can be deleted.

12. Once all samples have been optimized, open "Batch" from PeakNet main menu.

    a. Select input:

        1. Select schedule which you wish to batch.

        2. Lines used should be one less than total lines in schedule.

    b. Click output tab:

        1. Click on summary report.

c. Click export tab:

1. Type in name of download file, e.g.: G:\data\inorgani\ic\yymmdd A or B.

CALIBRATION AND STANDARDIZATION:

Perform calibration with standards at the following levels (ppm): 0.20, 1.0, 10, 15, 25 and 30. These standards define the linear range for the analysis. The correlation coefficient must be 0.995 or greater.

QUALITY CONTROL:

1. Initial Demonstration of Performance

The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

a. Linear Calibration Range (LCR) – The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ± 10%, linearity must be reestablished.

b. Quality Control Sample (QCS) – When beginning the use of this method, and on a quarterly basis verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within ± 10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before continuing with on-going analyses.

c. Method Detection Limit (MDL) – MDLs must be established for all anions, using reagent water fortified at a concentration of two to three times the estimated instrument detection limit. MDLs should be determined every six months, when a new operator begins work or whenever there is a significant change in the background or instrument response (see Appendix A).

2. Assessing Laboratory Performance

a. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of the day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. The experience of the analyst should weigh heavily in the interpretation of chromatograms.

b. Initial Calibration Verification (ICV)
The ICV must be analyzed immediately after calibration and meet the rejection criteria of ± 10% of the true value. Recalibrate if the ICV fails. The concentration of the ICV should be near the mid-point of the calibration curve.

c. APG Check Standard
An APG check standard for each anion must be analyzed weekly to check column efficiency, accuracy, etc. Acceptance criteria is ± 10% of the true value. If the APG fails, the separation column will be replaced or taken out of service until it can be cleaned. Results will be recorded in the IC Daily Log.

d. Initial Calibration Blank (ICB)
The ICB must be analyzed after the ICV. The absolute value must be ≤ EQL. Recalibrate if it fails.

e. Continuing Calibration Verification (CCV)
The CCV is analyzed after every 10 samples. Rejection criteria is ± 10% of true value. If the CCV fails, the problem must be corrected and the previous 10 samples between the CCV and last CCB must be reanalyzed. Concentration of the CCV should be near the mid-point of the calibration curve. As long as the CCVs that bracket the samples to be reported for the analytes of interest are within the acceptable limit, the run is acceptable.

f. Continuing Calibration Blank (CCB)
The CCB is analyzed after every CCV. The absolute value must be ≤ EQL. If the CCB fails, the problem must be corrected and the previous 10 samples between the last CCB and the CCV must be reanalyzed.

g. Laboratory Control Sample (LCS)
The LCS is carried through all preparation procedures and analyzed for each matrix type with a frequency of 5%. The LCS must be within ± 10% of the true value. See Appendix A for control limits. In cases where the LCS recovery is outside of the acceptable range, all samples prepared in that batch must be re-prepared and re-analyzed.

h. Method Blank (MB)
The MB is carried through all prep procedures and analyzed with a frequency of 5%. Rejection criteria is >EQL. Other criteria may apply, such as regulatory limit and the analyte concentration in the samples.

i. One matrix spike (MS) and one matrix spike duplicate (MSD) are analyzed for each group of samples that are similar in matrix at a frequency of 5%. If there are less than 20 samples in the analytical batch, a MS and MSD must be analyzed per batch. Both QC samples must be calculated for accuracy. See Appendix A for control limits.

$$\text{Spike Percent Recovery} = \frac{SSR - SR}{SA}$$

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

If both spike recoveries are outside of the specified control limit, the corresponding parent sample is to be diluted and MS/MSD performed.

Dilute appropriately until an acceptable recovery is obtained. If only the matrix spike OR the matrix spike duplicate is out of control for accuracy, then the corresponding parent sample is flagged with the MS qualifier.

If there is insufficient sample volume to perform a matrix spike and a matrix spike duplicate, an LCS and an LCS DUP must be used in its place.

j. Relative percent difference (RPD) between the MS/MSD is used to calculate compliance. See Appendix A for control limits.

Calculation:

$$RPD = \frac{|MS - MSD|}{(MS + MSD)/2} \times 100$$

MS = Method Spike Value
MSD = Method Spike Duplicate Value

If the RPD is outside of the acceptable control limits, the reported sample result is to be qualified with the * flag.

3. Sample Result Calculations:

Aqueous Sample Calculation:

Raw Data result (mg/L) X DF = Final Result (mg/L)

DF = Dilution Factor

SAFETY:

The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Laboratory staff should observe all safety procedures as outlined in the Laboratory Health and Safety Manual. Staff should consult Materials Safety Data Sheets (MSDS) for information on specific chemicals.

POLLUTION PREVENTION and WASTE MANAGEMENT:

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Laboratory staff should order and prepare only those quantities of reagents that will be used prior to the expiration date. Other appropriate measures to minimize waste generation should be brought to the attention of laboratory management. All laboratory waste shall be handled as directed by the Laboratory Waste Management Plan and Hazardous Waste Contingency Plan.

APPENDIX A
ION CHROMOTAGRAPHY QUALITY CONTROL LIMITS[a]

ANION	MDL (mg/L)	Reporting Limit (mg/L)	LCS Control Limit (% Rec)	MS/MSD Control Limit (% Rec)	RPD Control Limit (%)
Bromide	0.063	0.20	90-110	82-111	10
Fluoride	0.060	0.10	90-110	80-110	7
Chloride	0.076	2.0	90-110	65-129	12
Nitrate	0.13	0.20	90-110	90-110	6
Nitrite	0.077	0.20	90-110	85-110	6
Sulfate	0.072	2.0	90-110	66-111	5

[a] Laboratory Control Sample (LCS) determination, EPA Method 300.0, Revision 2.1, August 1993. Method detection limits, Reporting limits, MS/MSD and RPD control limits are updated periodically. The values currently in use may differ slightly from those published.